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TITLE: Thermally reversible isocyanate-based polymers

**BSPR:**  
Prior-art isocyanate-based polymers have been low molecular weight isocyanate compositions that afford good working properties, e.g., application ease, surface wettability and penetration, leveling ability, and gap-filling capacity. Such materials are commonly moisture-cured to form substituted polyureas after being applied to give durable coating or adhesive materials. However, such materials do not have the high performance characteristics of some of the more costly high-performance polymers such as the polyimides. Typically as one attempts to improve the performance characteristics of the isocyanate-based materials using conventional techniques, high-viscosity and associated low wettability result in a loss of substrate bonding ability. Currently conventional isocyanate polymers do not allow for the high temperature processing, e.g., soldering and thermoforming, of flexible circuit boards and other components such as chips, transformers and motors. Conventional isocyanate polymers typically do not provide cracking resistance at high enduse operating temperatures such as found in high performance aircraft, automotive and computer equipment. The processibility of high performance materials that are used in high performance protective dielectric film or coating materials is more limited than desired. A need continues to exist for a better, melt-processible, high-performance materials for molding and coating applications, especially finish surface coatings on composite materials.

**BSPR:**  
Often it is desirable to block the isocyanate functionality prior to its reaction with the labile hydrogen functionality so as to prevent unwanted irreversible reactions with moisture and other reactive hydrogen contaminants. As a result, improved handling and stability of the isocyanate functionality is obtained. By using a volatile blocking agent such as phenol, the blocked isocyanate can be reacted with the labile hydrogen functionality by heating the two reactants so as to unblock the isocyanate by vaporizing the phenol leaving the unblocked isocyanate to react with the labile hydrogen functionality.

**DEPR:**  
Preferrably the composition meeting this need is a polycarbonate oligomer with phenolic-hydroxyl end groups that forms a thermally-reversible urethane linkage with diphenylmethane diisocyanate (MDI). Trimethylolpropane is used to form thermally-reversible cross-links with the diisocyanate and polycarbonate oligomer. Polycaprolactone diol, p-phenylphenol, and bis-hydroquinone isophthalic acid diester may also be incorporated into this composition.

**DEPR:**  
To a clean flame-dried 250 ml Pyrex round-bottom flask was added 5.2 g (0.040 eq) Isonate 143L (80% diphenylmethane diisocyanate and 20% of its triisocyanate cycloadduct) from Upjohn's polymer chemicals and 3.8 g (0.040 eq) of phenol. The flask contents were gradually heated in an oil bath to 160.degree. C. under argon to obtain a uniform melt. Molten Nix polyol PCP-0200 (5.3 g, 0.020 eq) was gradually blended into the melt and the flask temperature maintained at 156.degree. C. during the addition. A yellow-white precipitate was noted after the addition which gradually remelted as the temperature was increased to 165.degree. C. Then 2.35 g (0.020 eq) of bisphenol A was melt blended into the melt. The temperature of the mixture was gradually increased to 240.degree. C. (464.degree. F.) to drive the equilibrium of the phenol/bisphenol A reaction in favor of reacting with bisphenol A and thus distilling off phenol. During this

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increase in temperature the melt became an orange-gold viscous liquid and most probably a prepolymer. In this way 2.0 g of phenol was distilled from the prepolymer melt over a 20 minute period. The product was a clear viscous melt which solidified when cooled to an insoluble, tough plastic with good adhesion to steel.

## DEPR:

Examples 1 and 2 were carried out using Upjohn's polyisocyanate Isonate 143L (80% diphenylmethane diisocyanate and 20% of its triisocyanate cycloadduct) and Union Carbide's Niox polyols PCP-0200 and PCP-0260 (polycaprolactone diols of varying DP). These proved quite successful. Initially, two equivalents of the Isonate 143L were blocked with two equivalents of phenol at 160.degree. C. to protect the isocyanate groups against hydrolysis. The phenol could then be selectively removed as needed by reaction with the aliphatic polydiols or by equilibration with polyphenols. Thus, molten PCP-0200 (Example 1) or PCP-0260 (Example 2) were gradually added to the blocked Isonate 143L/phenol product and the temperature maintained at 160.degree. C. Then with stirring, one equivalent of bisphenol A (relative to the aromatic phenol urethane groups) was added and the temperature of the mixture was gradually increased to about 240.degree. C. to drive the equilibrium of the phenol/bisphenol A reaction in favor of reacting with bisphenol A and removing phenol by distillation. The removal of nearly one equivalent of phenol in Examples 1 and 2 produced a bisphenol A extended, phenol end-capped Isonate 143L-PCP polyesterpolyurethane block copolymer.

## DEPR:

The polycaprolactone diol (PCP-530; Aldrich 18,940-5; 3,280 g), paraphenylphenol (PPP; Aldrich 13,434, 97%; 0.0180 g), bis-hydroquinone isophthalic acid diester oligomer (HQ/IPA/HQ, phenol end groups from Example 16; 1.696 g) and polycarbonate (PC; from Example 17; 0.580 g) were melted together while hand mixing with a stainless steel spatula in a 180 ml electrolytic (deep) beaker under an inert gas (argon) blanket at about 210.degree. C. Trimethylolpropane (TPM, 0.101 g) with a hydroxy equivalent weight of 44.7 was reacted in situ with 4,4'-diphenylmethane diisocyanate (crystalline MDI, Isonate 125M, Dow, mp 37.degree. C.; 3.116 g) with a hydroxy equivalent weight of 44.7 to give an aromatic triisocyanate that was added to the previous melt while the melt was stirred at about 150.degree. C. It was quickly incorporated in the melt and the viscosity increased to a fairly high level in about five minutes. The melt was heated to 180.degree. C. and the viscosity decreased to a very easily stirred level. Adhesive specimens were then hand assembled by applying melted adhesive to 0.5.times.1.0 inch areas (1.27.times.2.54 cm) on the ends of 1.times.3.times.0.032 inch (2.54.times.7.62.times.0.0813 cm) dull finish steel 1/4 hard (R-13) coupons (Q Panel Inc., Cleveland, Ohio). The steel test coupons had been hand cleaned/degreased first with a Kimwipe soaked with toluene, then one soaked with methyl alcohol, and preheated on a hot plate set at about 180.degree. C. surface temperature. The test samples were adjusted to give 0.5 in.sup.2 (3.23 cm.sup.2) contact area, firmly pressed together by hand, the excess adhesive exudate scraped away and the assembled test specimen clamped together with two, one-half inch (1.27 cm), spring loaded, IDL binder clips. One clip was placed on each side of the overlapped bond area. The partially cooled samples were then placed in a 200.degree. C. air oven briefly (3-5 minutes) to insure that the adhesive had flowed and contacted all the metal surfaces. The samples were then allowed to cool to ambient temperature and placed in a constant temperature/humidity (73.degree. F.; 22.8.degree. C., 20% relative humidity) room to condition for 24 hours prior to testing.

## DETL:

## TABLE 3

MELT ADHESIVE COMPOSITIONS AND LAP SHEAR STRENGTH.sup.(a) Lap Shear Composition										HOT	
Strength.sup.(j)	lb/in.sup.2	Number	PCP530.sup.(b)	HQ/IPA/HQ.sup.(c)	PPP.sup.(d)	PC.sup.(e)	CB75.sup.(f)	TMP.sup.(g)	MDI.sup.(h)	NDI.sup.(i)	(Pa .times. 10.sup.7)
3.315	2.134	0.0425	--	--	--	--	--	2.645	1820(1.25)	B	5.660 -- 0.0425 4.330 --
3.140	--	2760(1.90)	C	3.315	2.129	0.0425	--	--	3.140	--	2288(1.58) D 3.207
1.696	0.0360	0.433	--	--	2.814	--	2800(1.93)	E	3.207	1.696	0.0360 0.433 --
2.802	--	2790(1.92)	F	3.280	1.696	0.0360	0.433	0.073	--	2.802	-- 2575(1.78) G
3.280	1.696	0.0360	0.433	0.786	--	2.560	--	2350(1.62)	H	3.280	1.696 0.0180 0.580
--	0.101	3.116	--	3200(2.21)	I	3.280	1.148	0.0180	4.540	--	0.101 3.116 --
2820(1.94)	J	3.280	1.696	0.0180	0.580	--	0.101	3.116	--	3007(2.07)	K 3.280 1.696

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0.0180 0.580 -- 0.101 -- 2.617 2203(1.52)

.sup.(a) All components in g. Equal equivalent amounts of hydroxyl and isocyanate groups used in each composition. Compositions prepared by hand melt blending of diol/polyol/aromatic polyphenol components under an argo blanket, followed by addition of the aromatic di or trisocyanates. The preparation of composition C in described in Example 9. .sup.(b) PCP 530 = polycaprolactone diol, hydroxy equivalent weight 265 .sup.(c) HQ/IPA/HQ = bishydroquinone diester of isophthalic acid, preparation described in Example 5, hydroxy equivalent weight 170.2 .sup.(d) PPP = 4phenylphenol (pphenylphenol), hydroxy equivalent weight 170.2 .sup.(e) PC = polycarbonate based on bisphenol A and phosgene, with phenolic hydroxyl and groups and a degree of polymerization of approximately 9. Preparation described in Example 6, hydroxy equivalent weight 1258. .sup.(f) CB75 = Mondur CB75 triisocyanate crosslinker, isocyanate equivalent weight 323 (Mobay, based on trimethylolpropane reacted with 3 moles of toluene diisocyanate, TDI, to give an aromatic triisocyanate wit ortho methyl groups adjacent to each isocyanate). .sup.(g) TMP = trimethylolpropane, hydroxy equivalent weight 44.7 (react insitu with MDI to provide an aromatic triisocyanate crosslinker). .sup.(h) MDI = (4,4' diphenylmethane diisocyanate, isocyanate equivalent weight 125.1, Dow Isonate 125M). .sup.(i) NDI = (1,5 naphthalene diisocyanate, isocyanate equivalent weight 105.1, Mobay Desmodur 15). .sup.(j) Lap shear strength. Test samples assembled from 1 in .times. 3 i (2.54 .times. 7.62 cm) steel coupons (R13) from Q panel Inc, Cleveland, Ohio. Tensile test in Instron Floor Model TTE. Results are average values for three adhesive test specimens. Hot melt composition (180-210.degree. C.) hand applied to 1.0 .times. 0.5 in (2.54 .times. 1.27 cm) area of preheated (.about.180-200.degree. C.) steel coupon. Coupons firmly presse together and excess adhesive (exudate) scraped away. Assembled test samples then clamped together with two onehalf inch (1.27 cm), spring loaded, IDL binder clips. Heat quickly (.about.1 min) to .about.200.degree. C. in air oven then cool to ambient. Condition at 23.degree. C., 50 percent relative humidity for 24 hours before testing.

ORPL:  
Dieterich, D. et al., "Polyurethane Ionomers, A New class of Block Polymers",  
Angew. Chem. Internat. Edit., vol. 9, (1970), pp. 40-50.

ORPL:  
Wicks, Jr., Z. W. "New Developments in the Field of Block Isocyanates", In:  
Process in Organic Coatings, 9(1981), pp. 3-28.

ORPL:  
Yang, W. P., et al., "Thermal degradation of urethanes based on  
4,4'-diphenylmethane diisocyanate and 1,4-butanediol (MDI/BDO)", Polymer, vol.  
27, (Aug. 1986), pp. 1235-1240.

ORPL:  
Dieterich, D. et al. "Polyurethane Ionomers, A New Class of Block Polymers"  
Angew. Chem. Internat. Edit. vol. 9 (1970) pp. 40-50.

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